UNIVERSITY OF ALBERTA

X-RAY DIFFRACTION INVESTIGATION

OF

SILVER-COPPER EUTECTIC ALLOY AMALGAM

by

David Bruce Kerr Innes

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ABSTRACT

X-ray diffraction techniques have been used to identify the phases formed on the amalgamated surface of spherical particles of a silver-copper eutectic alloy (Ag-28.1 weight percent Cu). The results obtained from the diffraction patterns have been analyzed with the aid of an IBM 1620 computer and a comparison is made between the crystallographic parameters of the phases identified and parameters listed in the literature. It is concluded that the phases formed are CuHg and an Ag-Hg phase with a composition range from Ag_5Hg_8 to Ag_3Hg_4. These phases contribute to the bonding when conventional dental amalgam is dispersion strengthened by the addition of a silver-copper eutectic alloy powder. A discussion of the properties of dental amalgam is presented in relation to the phases formed and their modes of reaction under applied stress.

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X-ray diffraction techniques have been used to identify the phases formed on the amalgamated surface of spherical particles of a silver-copper eutectic alloy (Ag-28.1 weight percent Cu). The results obtained from the diffraction patterns have been analyzed with the aid of an IBM 1620 computer and a comparison is made between the crystallographic parameters of the phases identified and parameters listed in the literature. It is concluded that the phases formed are Cu$_3$Hg and an Ag-Hg phase with a composition range from Ag$_3$Hg$_6$ to Ag$_3$Hg$_4$. These phases contribute to the bonding when conventional dental amalgam is dispersion strengthened by the addition of a silver-copper eutectic alloy powder. A discussion of the properties of dental amalgam is presented in relation to the phases formed and their modes of reaction under applied stress.

ACKNOWLEDGEMENTS

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INTRODUCTION

For over one hundred years mercury alloys have been used as a dental restorative material. Dental amalgam offers the unique combination of convenience of use and favorable physical and mechanical properties, and these factors have led to its use in about 75% of all restorations[1]. However, the mechanical properties of amalgam are quite susceptible to variations in preparation techniques, and it is estimated that 40% of amalgam failures[2] are due to improper preparation.

Clinical studies[3,4] have shown that a large number of failures of amalgam restorations can be related to inadequate compressive strength of the material. In 1961 an investigation was undertaken to evaluate methods of improving the compressive strength of amalgam, with particular emphasis on the method of dispersion strengthening. As a result of this work, a dispersion strengthened amalgam, using an Ag-Cu eutectic alloy as the dispersed phase, was developed[5]. The new amalgam has strengths up to 30% higher than that of conventional amalgam.

Metallographic examination of dispersion strengthened amalgam clearly showed the presence of a bonding phase or phases between the Ag-Cu dispersion phase and the conventional amalgam matrix (see Figure 1). It was of interest to determine the composition and structure of the bonding phases at the interface. This investigation, using X-ray diffraction techniques, forms the basis of this thesis. A discussion of some properties of dental amalgam is also presented.
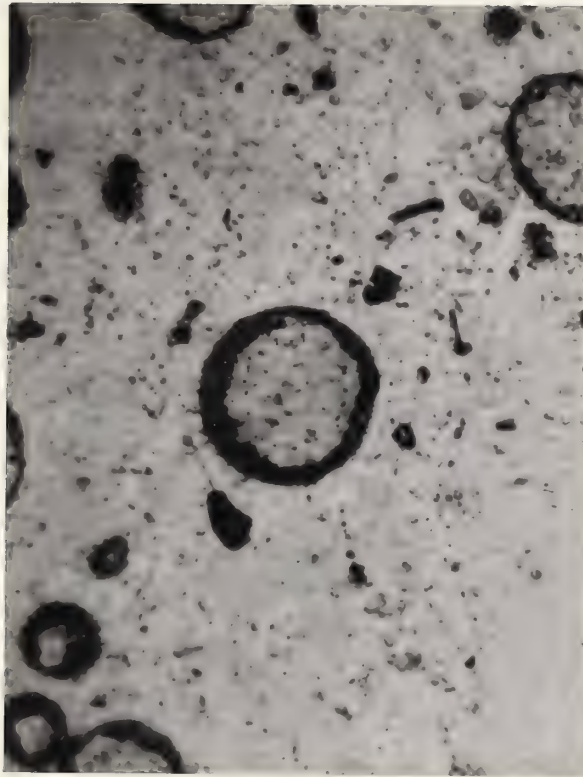
Figure 1. X1050

Bonding Phases in Dispersion Strengthened Amalgam

HISTORICAL REVIEW

Amalgam is the term used to denote any alloy of mercury. Conventional dental amalgam is prepared by mixing mercury with a comminuted Ag-Sn alloy containing a few percent of copper and zinc, the composition limits of which are set down by the American Dental Association[1]. The weight percentage* composition of a typical commercial dental alloy is 69.3% Ag - 26.3% Sn - 3.6% Cu - 0.8% Zn. It should be noted that the composition limits are specified only in lieu of a satisfactory tarnish and corrosion test to evaluate the alloys.

Recorded use of an amalgam in dentistry dates back to 1601, but because of the alleged toxicity of mercury there was no widespread use of amalgam as a restorative material until about 1900. By this time, enough clinical and experimental evidence had been acquired which showed that amalgam was relatively harmless to tissue. Much of the uncertainty in the preparation of dental amalgam was removed when Black[6] reported his study of the effect of alloy composition and manipulation on the properties of hardened dental amalgam. From the results of his investigation, he recommended a particular composition which he considered to be the most suitable for use in dental amalgam. The composition of his alloy is very similar to many of today's commercial alloys. His work established the foundation for subsequent researches in the preparation and properties of dental amalgam.

The first equilibrium diagram investigation of an alloy similar to the type developed by Black was done by Petrenko[7] in 1907; he described an

* Compositions are weight percent unless otherwise specified.

Ag-Sn phase which had a composition corresponding to Ag_3Sn. The presence of this compound was confirmed by McBain and Joyner[8] in 1912. By determining the limits of the liquid phases, and noting the position and shape of these regions, McBain and Joyner were able to deduce the composition of the equilibrium solid phases existing in contact with the liquid alloy. Their interpretations were based on available knowledge of the phase diagrams of Ag-Sn, Ag-Hg and Sn-Hg binary alloy systems. These phase diagrams were later shown to be incomplete, and in some cases, incorrect. McBain and Joyner also postulated the following reaction to account for the hardening in dental amalgam:

$$\gamma + 4Hg \rightarrow \gamma_1 + Sn, \qquad (1)$$
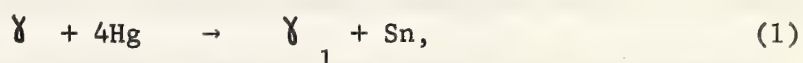
where $\gamma \equiv Ag_3Sn$ and $\gamma_1 \equiv Ag_3Hg_4$. Anomalies in cooling curves suggested that formation of a ternary phase was possible at temperatures above $70^\circ C$; however, in 1913 Knight and Joyner[9] concluded that no ternary compound of Ag, Sn and Hg formed at elevated temperatures. The transition phenomena noted were interpreted as rapid changes in solubility rather than a phase transformation. Gray[10] nevertheless, supported the phase transformation theory because the transition involved a large absorption of heat. He showed[11] in 1921 that the addition of zinc to the Ag-Sn alloy raised the transition region of the amalgam. Gray published further works[12,13] which discussed the effects of manipulation on the mechanical properties of amalgam, and proposed that expansion of amalgam on setting was due to crystal growth, while contraction "was caused by solution of dental amalgam alloy in mercury."

An accurate description of the amalgamation process in these alloys required the separate study of the binary alloy systems involved. In 1926

Murphy[14] published the complete equilibrium diagram for the Ag-Sn system with all phase boundaries delineated. In an appendix to Murphy's paper G.D. Preston's x-ray analysis of Ag_3Sn was included. Preston stated that the Ag_3Sn compound was close-packed hexagonal, with the parameter a=2.98 Å and the axial ratio c/a= 1.61. After a further study of the Ag-Sn system, Nial, Almin and Westgren[15] concluded that Ag_3Sn was actually orthorhombic with parameters a_1 = 2.985-2.994 Å, a_2 = 5.144-5.154 Å, and a_3 = 4.771 Å over a composition range 24.0 to 25.5 atomic percent tin.

The equilibrium diagram for Ag-Hg alloys was published by Murphy[16] in 1931 and included another appendix by Preston on the x-ray diffraction analysis of the system. The most important phase identified was γ_1, a body-centered cubic structure (complex, gamma brass type) with the parameter a = 10.0 Å. Murphy suggested that this phase had a stoichiometric composition corresponding to the compound Ag_5Hg_8 rather than Ag_3Hg_4 as proposed by McBain and Joyner (c.f. equation (1)). In any case Murphy concluded that the γ_1 phase of the Ag-Hg system was the principal compound formed in an amalgamated Ag_3Sn type alloy. The β_1 phase was found to be a close-packed hexagonal structure with parameters a = 2.964 - 2.987 Å and c = 4.830 Å and a composition Ag_5Hg_4.

A limited study of the Sn-Hg system was made by von Simson[17] in 1924. Using x-ray diffraction methods she determined the solubility of mercury in β-tin (tetragonal form) and showed the existence of a simple hexagonal $Sn_{7-8}Hg$ phase in the region beyond six atomic percent mercury. The extent of this phase, called γ_2, was supported by Stenbeck's investigation[18] of 1933, although he did not publish any experimental data.

With complete descriptions available of the three principal binary systems involved in the amalgamation reactions, a more detailed analysis

of the reaction was possible. Gayler[19,20] published two papers in 1937 in which the constitution of ternary Ag-Sn-Hg alloys, and a theory to account for hardening and volume changes in amalgam were presented. The setting reactions postulated by Gayler were based on metallographic, thermal, and x-ray analysis of the Ag-Sn-Hg system. It is important to note that in two instances the metallographic results contradicted the x-ray results. She proposed the following two part equilibrium setting reaction:

$$\gamma + Hg \rightarrow \beta_1 + \gamma_2 \quad , \tag{2}$$

$$\beta_1 + \gamma_2 \rightarrow \beta_1 + \gamma_1 + \gamma_2. \tag{3}$$
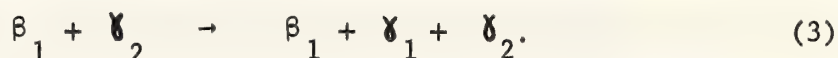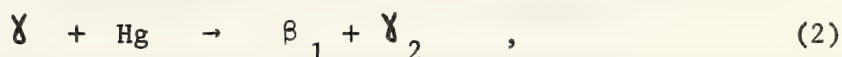
These reactions showed that tin did not separate as a product of the reaction (c.f. equation (1)).

At the same time that Gayler was publishing her results, Troiano[21] was completing an extensive x-ray examination of dental amalgam. He generally confirmed Gayler's constitutional diagram but suggested a different sequence in the setting reactions:

$$\gamma + Hg \rightarrow \gamma_1 + \delta_2 + \text{unattacked } \gamma \quad , \tag{4}$$
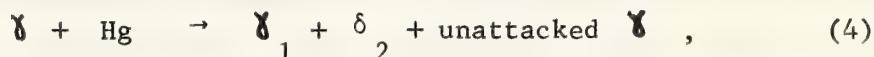
where $\delta_2 \equiv HgSn_3$. At this point the solid-liquid reaction terminates and Troiano proposed that any further changes occurred in the solid state:

$$\gamma_1 + \delta_2 + \text{unattacked } \gamma \rightarrow \gamma_1 + \gamma_2 \rightarrow \beta_1 + \gamma_2 + \gamma_1 \tag{5}$$
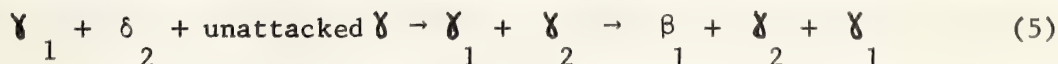
However, Troiano could not find any evidence of the last stage of reaction (5), and this contradicted Gayler's contraction theory which involved the formation of β_1.

Gayler, in the discussion of Troiano's paper, disputed the presence of the δ_2 phase and later works[24] identified the phase as the simple hexagonal γ_2 compound. Troiano also suggested that the volume changes during setting were the result of reactions between the solid and liquid phases.

X-ray diffraction studies of the structure of the γ_1 compound and the α_1 solid solution of the Ag-Hg system were reported by Berman and Harcourt[22] in 1938. They established γ_1 to be body-centered cubic with a = 10.1 Å, a space group Im3m with a unit cell $Ag_{20}Hg_{30}$, and named it "Moschellandsbergite." The data for this phase have been listed as 2-1103 in the Index of the A.S.T.M. X-Ray Powder Data File for 1957, but later editions of the file (1960) omit this information. The significance of this omission is not fully understood.

The variation in lattice parameter of the γ_1 phase as reported by different workers, can be attributed to the composition range (about 2%) of the compound.

No additional structural work appeared until 1960 when Fairhurst and Ryge[23] identified the γ_2 phase as the only Sn-Hg phase that could form in amalgam at room temperature. Parameters of the simple hexagonal cell were determined to be c=2.995 - 2.984 $\pm$ 0.001 Å with c/a = 0.931; the Sn:Hg ratio varied from Sn_7Hg to Sn_8Hg.

Several other workers used x-ray diffraction techniques[24], recording x-ray spectrometers[24,25], and compression tests to determine the relative amounts of the various phases formed in amalgam, as a function of mixing time and manipulation methods. The relation of the rates of formation of phases to initial and residual mercury content was also studied. Winterhager and Dreiner[26,27] used recording x-ray spectrometers to study rate of phase formation in dental amalgam. They determined the half-life time and rate constant

governing the reaction for several compositions and methods of preparation.

Until 1963 no significant changes had been made in the composition of the alloy that Black originally recommended for use in dental amalgam. The strengths of the amalgams derived from these alloys have probably reached their optimum, and further improvement involved the application of an entirely new principle of alloy strengthening.

As noted earlier, the first departure from conventional amalgam used the principle of dispersion strengthening. Experiments by this author indicated that a particular dispersion strengthened amalgam had an ultimate compressive strength of about 64,000 pounds per square inch (psi) compared with strengths of 47,000 and 53,500 psi. for two commercial amalgams prepared under standard conditions.[1, 28]

The early development of this type of amalgam involved a large number of compression and flow tests to determine the optimum size of the powder and the maximum amount that could be added to the amalgam in order that the greatest increase in strength be achieved. A large decrease in the flow of amalgam was also obtained with dispersion strengthened amalgam. This flow rate is 0.53% in 21 hours.

The experimental amalgam uses a conventional dental amalgam alloy as the base to which is added 33.3% Ag-Cu eutectic alloy powder (-500 mesh). This mixture of alloy powders is amalgamated with an equal weight of mercury and triturated (mixed) for twenty seconds. Biological tests carried out by the Faculty of Dentistry at the University of Alberta in Edmonton have shown that this amalgam is non-toxic. This amalgam has been used successfully for nearly one year in the public dental clinic of the Faculty of Dentistry.

DISPERSION STRENGTHENING

In general, the addition of a finely divided second phase to a
crystalline matrix produces an alloy which is considerably stronger than
the matrix alone.[29]   The interaction of dislocations with the particles of
the second phase causes the strengthening, and this implies that either the
particle itself, or the interface between the particle and the matrix, is
acting to inhibit dislocation movement. Neglecting the effect of the inter-
face, the particle may act to strengthen in two ways. Firstly, if the dis-
persed particles are very close together, the dislocation is not able to
bow out and loop around the dispersion particles and is effectively blocked.
Secondly, if the interparticle distance is relatively large the dislocation
will be forced to climb over the dispersion particle, requiring more energy
to move the dislocation. If the Burger's vector of the partial dislocat-
ions formed during the climb does not lie in the plane of the stacking fault,
the partial dislocations become immobile (sessile) and a further strengthen-
ing effect occurs. The combination of these interactions plays a consider-
able role in strengthening the alloy.

The interface between the dispersed phase and the matrix can inhibit
dislocation movement in two ways. Firstly, if a coherent interface forms
between the dispersion phase and the matrix phase, a stress field will be
set up along the interface because of the slight changes in interatomic dis-
tances. This stress field tends to repel dislocations which have the same
type of stress field associated with them, or to annihilate dislocations of
opposite stress fields. Secondly, the dispersed phase may be bonded to the
matrix by phases which are contiguous to both; coherency effects may also be
associated with the bonding phases. The interfacial zones may inhibit

completely the movement of dislocations or else transmit them into the tougher dispersion particle.

Plastic yielding of the material occurs as long as the dislocations are able to move appreciable distances. However, as the dislocations pile up around a dispersion particle, back stresses result which eventually reduce the effective stress on the dislocation source. Yielding will stop unless the stress on the material is increased, and when the stress on the dispersion particle is sufficiently high, the particle will shear, and fracture of the material results. The fracture mode of amalgam will be discussed in a later section.

EXPERIMENTAL METHODS

1. PRODUCTION OF METAL POWDER BY ATOMIZATION

A special atomization process was developed to obtain sufficient quantities of the Ag-Cu eutectic alloy powder. The design of the atomizer is basically an adaption of commercial units which use a conical arrangement of atomizing jets. The arrangement of the atomizing jets is generally dependent on the size of the product powder desired and two rough rules are followed:

(1) For a given gas pressure, the greater the number of atomizing jets the closer will be the size range of the product powder.

(2) For a given number of atomizing jets, the higher the gas pressure the smaller will be the average size of the product powder.

If it was desired to get large amounts of very small powder, one would ideally build an atomizer body with an annular ring orifice and use infinite gas pressure. This was our desire, but for technical reasons the atomizer body constructed here has eight jets mounted concentrically at 65° - to the horizontal - on the atomizer body. (See Figs. 2-4). The jet streams are guided through brass tubes (orifice diameter = 0.043 in.) to about one-half inch away from intersection point (area of atomization) of the streams. These tubes are soldered onto the brass atomizer body and are aligned each time the atomizer is operated. The atomizer body has two gas inlet holes, a central hole down through which the metal stream passes from the holding furnace to the atomization area, and four blind holes which are used to mount the atomizer body to the holding furnace. A copper cooling

jacket is also soldered onto the top surface of the atomizer body.

The holding furnace is resistance heated and has a bottom pouring graphite crucible which is plugged with a graphite rod. The exit hole diameter, i.e. the diameter of the metal stream, is 0.028 in. (#70 drill).

In order to collect the powder, the furnace and atomizer body assembly are set on top of an open ended cylindrical tank 30" diameter x 36" high which itself sits in a square tray 31" x 31" x 6" deep and which contains about 3" of water. A truncated cone is concentrically mounted inside the cylindrical tank to stop the gases from blowing the fine powder upwards.

In operation, the furnace is preheated to about 875°C and the molten AgCu alloy - previously melted in a high-frequency unit - introduced. When the gas valves are opened and the pressure built up to 100 psig, the furnace plug is removed to allow the metal to drain continuously and uniformly and the resulting atomized metal collects in the water at the bottom of the tank. At the end of the atomization, the furnace and tank, etc. are lifted out of the tray and the water pumped out. The powder slurry is washed into a smaller container and dried under heat lamps. In the case of the silver-copper eutectic alloy, the powder particles are spherical in shape.

There is an oxide film left on the atomized powder which can be removed by heating the powder to about 200°C in a very slowly flowing hydrogen stream.

The powder is then screened and the fractions larger than 400 mesh (greater than 38 microns) are remelted and reatomized. Generally, between 17 and 22% of the powder passes 400 mesh. Analysis has shown the oxidation loss of copper to be negligible.
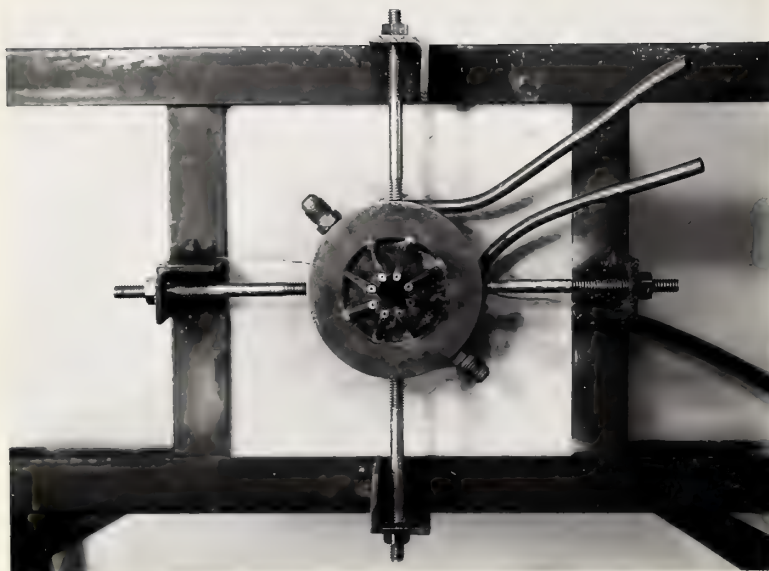
Figure 2.   Bottom of furnace showing mounted atomizer body.

Section

Section

FIGURE 3

1/4" N.C.

1/8" N.P.T.

Metal From Furnace

Gas Inlet

0.043" I.D.
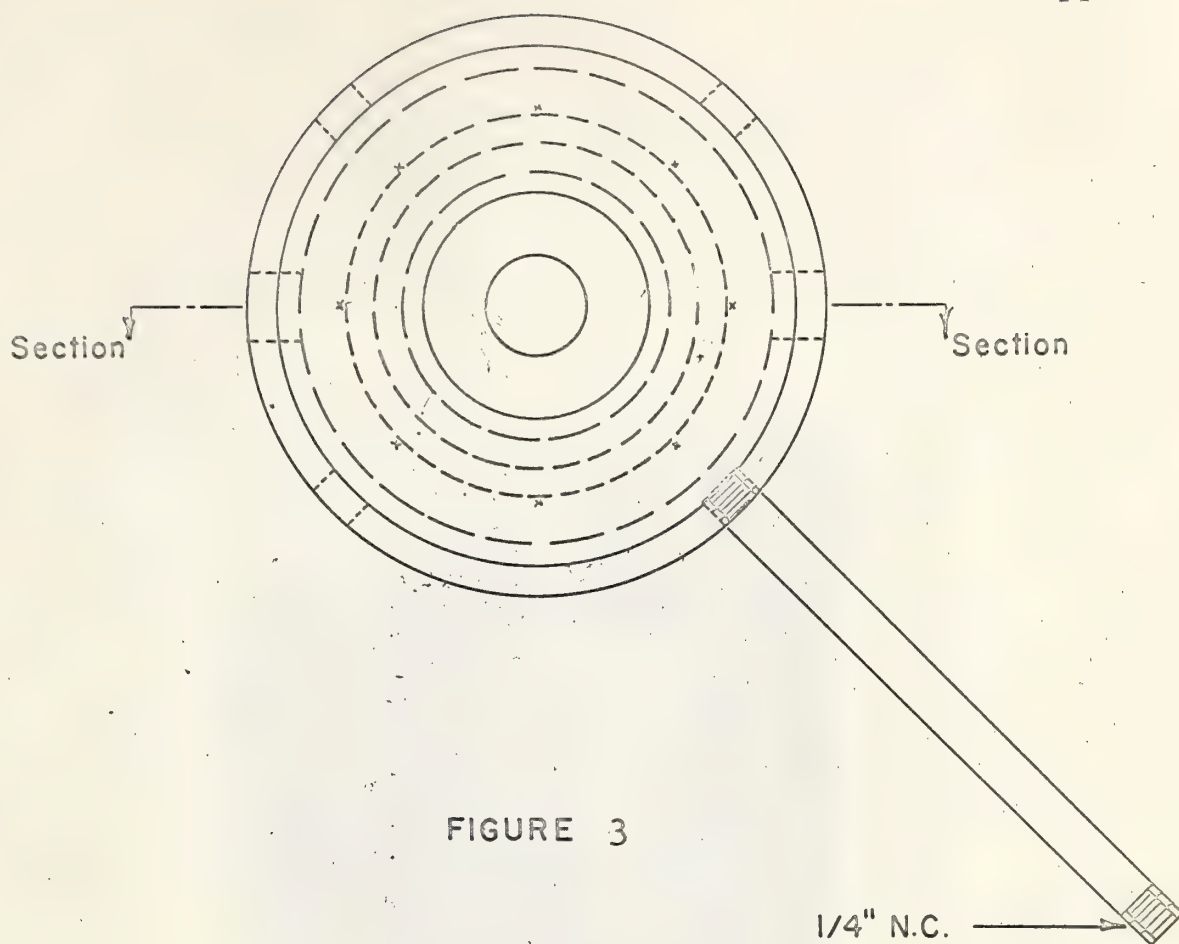
X
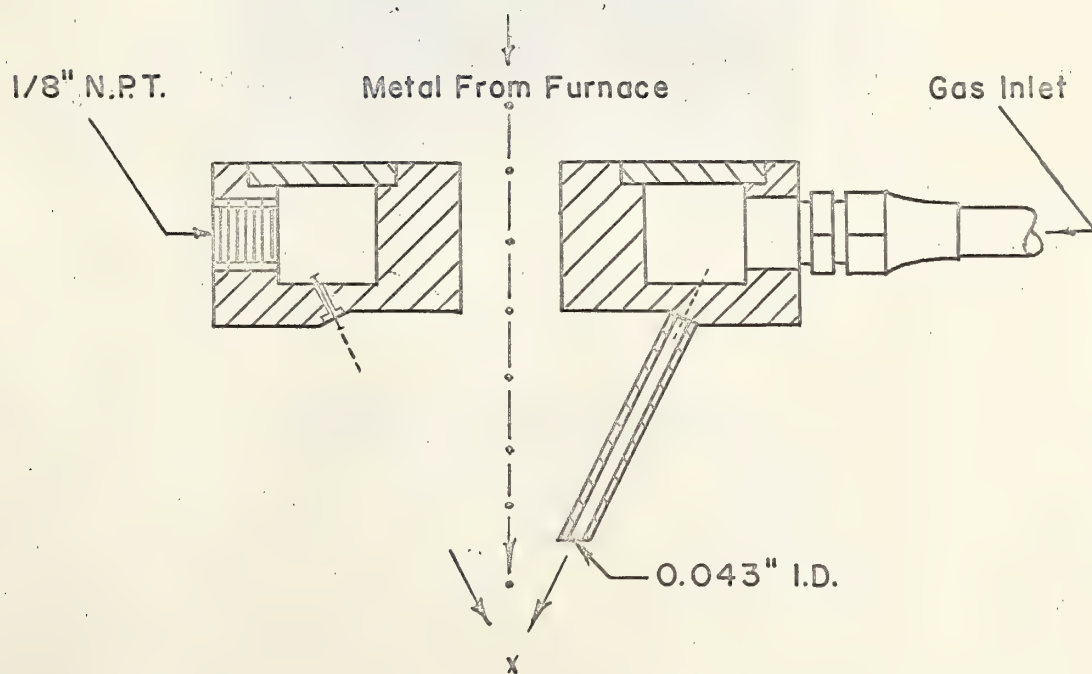
SCALE : full size

Figure 4.   Atomizer Assembly

TABLE 1

SCREEN ANALYSIS OF AN ATOMIZED
SILVER-COPPER ALLOY (EUTECTIC)

Size	Recovered(grams)	%
+ 325 mesh	1060	73.7
-325 + 400 mesh	63	4.4
-400 + 500 mesh	169	11.6
- 500 mesh	148	10.3
Total	1439	100.0

Note: 325 mesh = 44 microns
400 mesh = 36 microns
500 mesh = 27 microns

2. AMALGAM SAMPLE PREPARATION

To reduce the complexity of the problem of determining the phases which formed, the Ag-Cu alloy was amalgamated separately from the matrix. A sample was prepared by thoroughly mixing for at least fifteen minutes, with a mortar and pestle, equal weights of -27 micron Ag-Cu powder and mercury. The amalgam was then allowed to set for one week at room temperature. After this setting period, a filed powder sample of the amalgam was used for the x-ray investigation.

3. X-RAY INVESTIGATION AND DATA PROCESSING

A 57.3 mm. radius Debye-Scheerer powder camera and filtered (Ni) copper radiation were used to obtain the diffraction patterns of the amalgamated Ag-Cu powder. The strip photograph was indexed and values of 2θ and (h k l) were entered in a lattice parameter calculation program (Appendix 1.) and processed by an IBM 1620 computer. The output data consisted of a lattice parameter and a corresponding Nelson-Riley extrapolation function number for each reflection entered. These output data were then analyzed by the computer using a program for Cohen's Least Square Analysis. This operation yielded the best extrapolated lattice parameter from the data entered.

4. METALLOGRAPHY

For the first few hours after amalgamation the product phases are still in the process of growth. During this period the amalgam is quite soft and easily etched in warm water. As the material hardens its nobility increases rapidly and after a few days 25-50% aqueous HNO_3 must be used as

the etchant. To bring out the unattacked (by the mercury) portions of the γ phase, strong aqueous HCl must be used. It is necessary to experiment with the concentrations of the acid for each particular material; a dilute mixture of HNO_3 and HCl is often useful.

Polishing techniques for amalgam are not critical except that the final polish should be carried out on a clean, napless cloth to preserve the softer constituents. Alcohol may be used as the cutting fluid to reduce the possibility of a water etch. Samples are mounted in a thermoplastic material which requires no external heat or pressure to set. It is not desirable to mount amalgam in bakelite or lucite since the temperature required for setting will cause some decomposition of the mercury phases and release poisonous mercury vapor.

RESULTS AND DISCUSSION

1. INTERPRETATION OF X-RAY DATA

It was assumed that the powder photograph would show reflections from
the γ_1 and β- copper phases. This deduction was based on the structure of
the Ag-Cu alloy; the eutectic alloy solidifies in a lamellar form (see Fig-
ure 5) with alternating plates of silver-rich α and copper-rich β areas.
The alloy powder was deoxidized in an hydrogen gas atmosphere before amal-
gamating, but it was not possible to prevent slight reoxidation when the
cleaned powder was exposed to the atmosphere. Silver oxide did not seen
to inhibit amalgamation of silver powder but since copper oxide is more ten-
acious, it was expected that the β lamella would not be amalgamated. Further-
more, it was not expected that any primary α reflections would be present be-
cause the method of preparation assured virtually 100% amalgamation of the
α phase. Since the Ag-Cu powder was very much finer than the grooves of
the file, the filed particles would tend to break away from the amalgam
mass rather than shear.

Analysis of the reflections on the powder photograph showed that the
principal phase formed was γ_1. The reflections were compared with data
from a powder photograph of an Ag-71.0% Hg amalgam which corresponds to the
composition of the γ_1 phase. This amalgam was prepared by thoroughly mix-
ing the stoichiometric quantities of silver and mercury, and the material
was allowed to set for two months at room temperature. A comparison of these
data was also made with the data published by Murphy[16]. It is interesting to
note that Murphy's data include a value of $h^2 + k^2 + l^2 = 124$. This is an
impossible reflection from cubic lattices and was neglected.
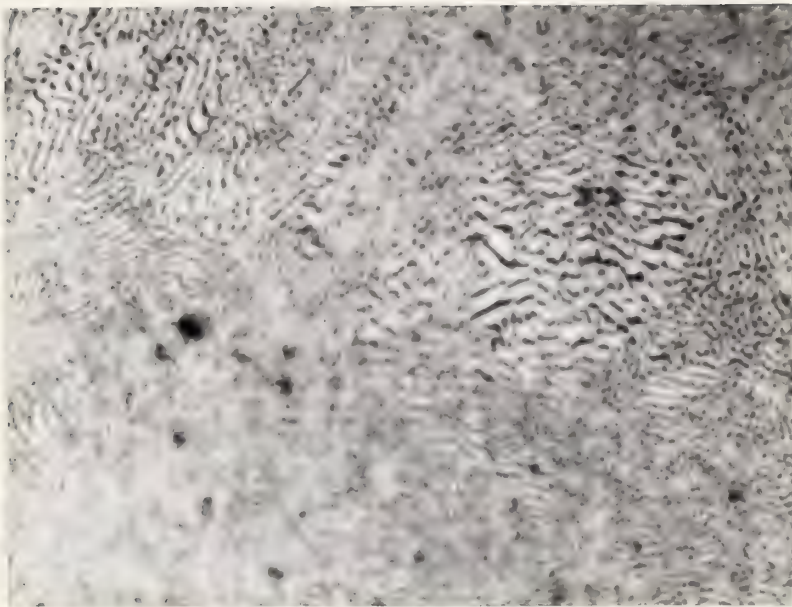
Figure 5. Silver-Copper Eutectic Alloy X1050

The comparison of the reflections of the amalgamated Ag-Cu alloy with other data left six low angle reflections unaccounted for. The numerical relationships between these lines indicated that they belonged to the CuHg phase (A.S.T.M. data file 4-0811) but the calculated lattice parameter a = 9.1 Å was somewhat lower than the given parameter a = 9.415 Å. To determine conclusively if the six low angle reflections were from the CuHg phase, a Cu-Hg alloy was prepared by mixing -325 mesh copper powder with mercury in a dilute aqueous solution of HCl. X-ray examination of this alloy showed the presence of primary copper reflections and reflections of the complex cubic CuHg phase. A comparison of certain of the low angle reflections of the CuHg phase with the unknown low angle reflections from the amalgamated Ag-Cu eutectic alloy indicated that the unknown reflections belonged to the CuHg phase. Lattice parameters calculated for individual corresponding reflections of the two materials compare almost exactly.

The presence of the CuHg phase in the amalgamated Ag-Cu alloy showed that the copper oxide film was broken down during the mixing of the amalgam. The presence of oxides or other films on a metallic surface does not assure permanent non-wetting.[30] Many liquid metals will, in due course, lift the oxide layer from the base metal after having diffused through the film or some defect in the film.

All pertinent x-ray data are presented in Appendix 2. In addition, Figure 6 is a composite of the x-ray powder photographs of γ_1, CuHg and amalgamated Ag-Cu alloy. The photograph shows the low angle lines which are of interest to this discussion; they are numbered one to six in order of increasing reflection angle. The top powder photograph is γ_1, the center photograph is the amalgamated Ag-Cu eutectic alloy and the bottom photograph is the CuHg phase from amalgamated copper powder.
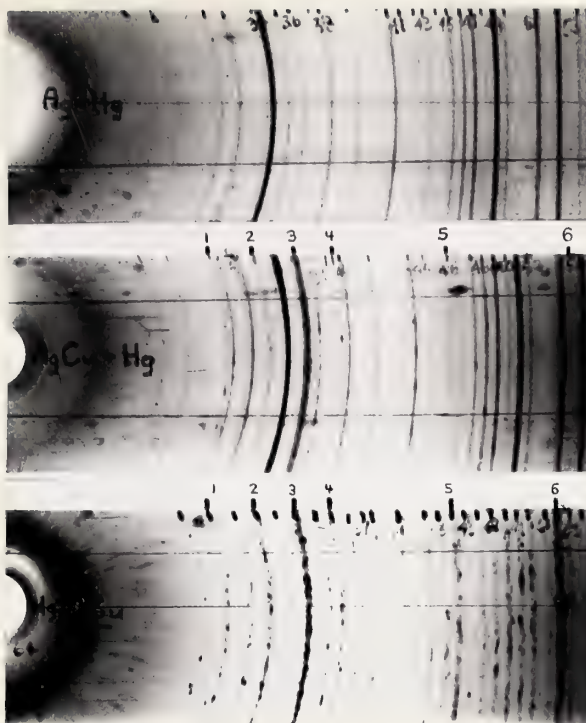
Figure 6

X-Ray Powder Photographs
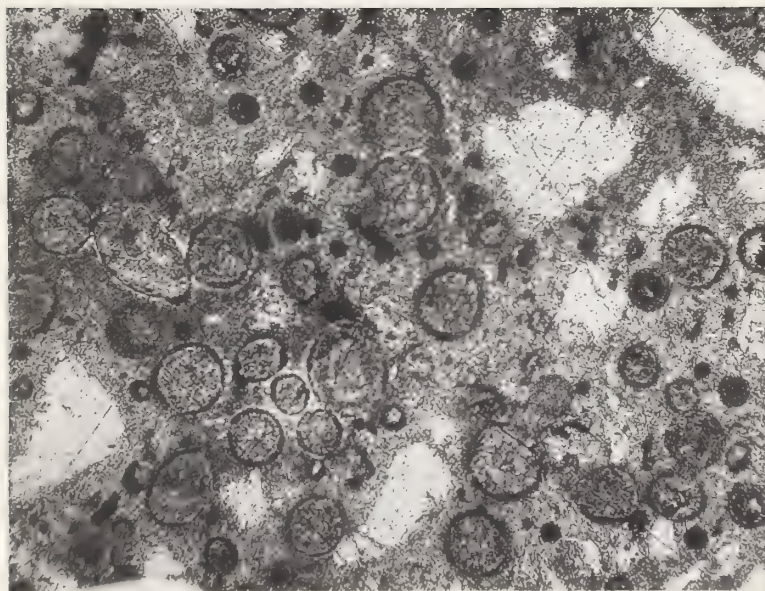
Figure 7. X550

Dispersion Strengthened Amalgam

2. METALLOGRAPHY

Figure 7. is a photomicrograph of a dispersion strengthened amalgam. The irregular-shaped particles are unattacked γ, the circular particles are of the Ag-Cu eutectic dispersion phase and the remainder is made up of γ_1 and γ_2.

3. PHASE FORMATION

It is possible to discuss phase formation in dental amalgam quali-tatively from a diffusion standpoint. No information is available on the diffusion rates of mercury in Ag_3Sn compound or the Ag-Cu eutectic phase, but a rough estimate can be made using the diffusion data obtained from Ag-Hg, Sn-Hg and Cu-Hg diffusion couples[31]. At room temperature the dif-fusion constant for the diffusion of liquid mercury into pure solid silver, tin or copper is of the order of 10^{-27} cm^2/sec. The smallness of this con-stant clearly eliminates the possibility of any significant amount of mer-cury diffusion into the solids. This means that the initial reaction rate will be controlled by the diffusion rate of silver, tin and copper into the liquid mercury. The initial diffusion rate will be relatively fast because of the infinite concentration gradients that exist. However, the room temp-erature solubility[32] of silver, tin and copper in mercury is only 0.04, 0.62 and 0.30% respectively, so that almost as soon as the reaction begins, phases will precipitate at the solid-liquid interface. The diffusion rate is then governed by the rate of breakdown of the interface phases, through abrasion by mixing, or if the surface phases remain intact, the diffusion rate of mercury through them. It is known that diffusion mechanisms in compound phases similar to γ and γ_1 are more complicated and the corresponding

diffusion rates somewhat lower than in pure metals[33].

Inspection of the Ag-Hg and Sn-Hg[34] equilibrium diagrams indicates that the first phases to form at the solid-liquid interface would be γ_1 and γ_2. It is reasonable to assume that these would be the only phases possible at the liquid interface, and that other Ag-Hg or Sn-Hg phases would have to form in the solid state. However, diffusion rates in the solid state at room temperature preclude this latter possibility. On this basis, it is unlikely that the β_1 phase would form in dental amalgam, and this hypothesis is consistent with the products formed in the second stage of the second reaction postulated by Troiano (c.f. equation (5)).

Formation of the CuHg phase in a Cu-Hg amalgam is slow because of the tenacious oxide film present on the surface of the copper particles. As was mentioned earlier, the Cu-Hg amalgam was prepared in solution and although it appeared that the copper particles were wetted quickly by the mercury, x-ray powder photographs taken two and six hours after amalgamation (the amalgam was still plastic) showed only a few very faint reflections besides those of copper. Eighteen hours after amalgamation the mass had become very hard and an x-ray powder photograph showed reflections of a new phase (CuHg) as well as faint reflections from the copper. The setting rate of the CuHg phase is somewhat slower than the rates suggested[26,27] for the γ_1 and γ_2 phases, and this is supported by clinical tests which show that the dispersion strengthened amalgam sets initially at a slightly slower rate than other types of amalgam.

4. DEFORMATION AND FRACTURE MODE OF AMALGAM

In the preceding sections of this report, the phases formed in dental amalgam have been described according to their stoichiometric compositions.

In discussing plastic deformation of this material, we must discuss the phases from the point of view of their crystallographic structures.

The δ_1 and CuHg phases both have a complex cubic (gamma brass type) structure probably containing 52 atoms per unit cell. In the Hume-Rothery[35] classification these phases should have an electron to atom ratio of 21:13. The δ and δ_2 phases are respectively orthorhombic and simple hexagonal and these phases are generally classified according to their atom ratios, i.e. AB, AB_2, AB_3... As a group, the δ, δ_1, δ_2 and CuHg phases fall in a general category called intermetallic compounds.

Research on intermetallic compounds has not been very extensive and little systematic knowledge of the properties and mechanical behavior, especially in the bulk state, is available. The principal features of high hardness and brittle character relative to the component elements are well known, and it is only recently that extrusion and simple fabrication techniques have been successfully developed[36]. It is also known that many intermetallic compounds exhibit a transition temperature, usually around 88% of the melting point ($^\circ$ K), where the hardness drops rapidly and the fracture mode becomes ductile.

Mechanical strengths of intermetallic compounds appear to be greatly affected by the degree of order of the crystal structure. Order, domain and defect phenomena have been suggested as possible approaches for improving or modifying the strengths of intermetallic compounds[36]. Strength has been observed to increase as the long range order decreases. Domain boundaries (enclosing regions of long range order) increase the resistance to slip because the slip creates additional anti-phase boundary[36], requiring more energy to be expended. The terms anti-phase boundary and domain boundary are synonomous. The presence of anti-phase boundaries inhibits

Frank-Read dislocation sources and also hinders the climb of dislocations.
Interaction of vacancies with moving pairs of dislocations results in
strings of atoms behind each dislocation pair and which will be in anti-
phase position within an ordered domain. Further motion will be resisted.
An explanation of the increasing ductility of intermetallic compounds as the
temperature increases may be that anti-phase domain structures are unstable
and may be thermally activated to move to lower energy (larger) domains.

The complexity of the structure of these compounds makes the slip
systems equally complex and little is known of the slip systems that are
operative. Dental amalgam is an aggregate of several different intermet-
allic compounds and it is unlikely that anything except a brittle fracture
could be expected in conventional amalgams. The presence of a dispersion
phase would have an additional effect on the fracture mode[37]. In a gener-
ally ductile matrix, the dispersion particles are sites of high local stress
concentrations which inhibit mobility of dislocations. Rapid work harden-
ing of the alloy would occur and there would be a strong tendency for
cracks to nucleate around the dispersion particles.

In a brittle matrix such as dental amalgam in which the dislocation
mobility is restricted even without a second phase, the addition of a tough
dispersion phase can act to increase the ductility of the alloy. This
anomaly occurs because the more ductile dispersion particles, in this case
the Ag-Cu eutectic phase, serve to dissipate stress concentrations and re-
duce crack velocity and propagation. At the very least, the ductile disper-
sion phase will allow some yielding to occur before fracture. This hypothesis
is in agreement with an observed increase in ductility of dispersion strength-
ened amalgam.

CONCLUSIONS

From the data presented it is concluded that the phases which bond the Ag-Cu eutectic alloy to the conventional dental amalgam matrix in dispersion strengthened amalgam are γ_1 and CuHg intermetallic compounds. Good correlation of experimental data is obtained for the x-ray powder photograph reflections from silver and copper amalgam with reflections from the amalgamated Ag-Cu eutectic alloy. The Nelson-Riley extrapolation function has been used for extrapolation of lattice parameters because it is valid over a wider range of angles than some other functions.

No attempt has been made in this work to determine equilibrium values of lattice parameters. The lattice parameters calculated agree reasonably well with values published in the literature. Published values of the lattice parameter of γ_1 range from 9.98 to 10.1 A and this variation is in agreement with the known composition range of γ_1.

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     Alloys". Institute of Metals Monograph No. 1 1956.

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     Compounds" Wiley, 1960.

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APPENDIX 1.

Lattice parameter calculation and extrapolation function program and least square analysis program in Fortram II language suitable for IBM 1620 computers.

For purposes of reproducing these programs, it was necessary to delete any information in location 1. on the IBM data cards. The first printed information corresponds to location 2. on the cards. To use either of these programs, the instruction ..1 is entered into the first three locations of the first data card. So, the first line (which represents the data on the first card) becomes:

..1 D.INNES LATTICE PARAMETER CALCULATION etc.

```
.    D.INNES LATTICE PARAMETER CALCULATION AND N-R EXTRAPOLATION FUNCTION
     922105   SAVE CARDS
.LOAD FORTRAN EXECUTE DUMP
10     FORMAT(4I2,2XF7.3)
12     FORMAT(2F20.10)
1      READ 10,I,J,K,L,S
       WL1=1.54050
       WL2=1.54433
       WL3=1.54178
       S1=3.14159265*S/360.
       S=SIN(S1)
       C=COS(S1)
       X=J*J+K*K+L*L
       SS=S*S
       SX=SS/X
       IF(I-1)2,3,4
2      WL=WL1
       GO TO 5
3      WL=WL2
       GO TO 5
4      WL=WL3
  7    FORMAT(3F20.10)
  5    D=0.25*WL*WL/SX
       D=SQRT(D)
       R=0.5*C*C*(1.0/S+1.0/S1)
       PUNCH 12,R,D
       GO TO 1
       END
```

```
   .    D.INNES LEAST SQUARES ANALYSIS 922105    SAVE CARDS
   .LOAD FORTRAN EXECUTE DUMP
         DIMENSION IX(100),IY(100)
    5    FORMAT(2F20.10)
   52    FORMAT(1X2E16.9)
  100    FORMAT(7I5)
    1    READ 50,N
   50    FORMAT(1XI4)
         SX=0.0
         SXX=0.0
         SY=0.0
         SYY=0.0
         SXY=0.0
         FN=N
         DO 10 J=1,N
         READ 5,X,Y
         SX=SX+X
         SXX=SXX+X*X
         SY=SY+Y
         SYY=SYY+Y*Y
         SXY=SXY+X*Y
   10    CONTINUE
         DEN=1.0/(FN*SXX-SX*SX)
         PUNCH 52,SX,SXX
         PUNCH 52,SY,SYY
         PUNCH 52,SXY,DEN
         A=(SY*SXX-SX*SXY)*DEN
         B=(FN*SXY-SY*SX)*DEN
         SD=(SYY-A*SY-B*SXY)/FN
         SB=SD*DEN*FN
         SA=SD*SXX*DEN
         PUNCH 53
   53    FORMAT(50H LEAST SQUARES ANALYSIS                          )
         PUNCH 54,A,SA
   54    FORMAT(5X2HA=,E16.9,5H(+OR-,E16.9,1H))
         PUNCH 55,B,SB
   55    FORMAT(5X2HB=,E16.9,5H(+OR-,E16.9,1H))
         PUNCH 56
   56    FORMAT(50H    Y=B*X+A                                      )
         GO TO 1
         END
```

APPENDIX 2.

The x-ray data, for each phase or element that has been investigated, is printed in three consecutive sections:

1. Diffraction data input.

    The first digit (0, 1 or 2) represents the wavelength of the radiation, the next three digits are the (hkl) values of the reflection and the number following is the reflection angle (two theta).

2. Parameter output, least squares analysis input.

    This data follows the diffraction data input. The first column of numbers are Nelson-Riley extrapolation functions and the second column of numbers are lattice parameters; each pair of numbers on a given line are output data from the lattice parameter calculation of any given input reflection. These data are the least squares analysis input.

3. Least squares analysis output.

    This output is in the form of a straight line equation

    $$Y = BX + A$$

    where A is the ordinate intercept and represents the extrapolated lattice parameter.

.   DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
GAMMA ONE (AGHG) FROM AGCU+HG

```
2  7  1  0     67.458
2  7  2  1     70.378
2  6  4  2     71.828
2  7  3  2     76.130
2  8  1  1     78.962
2  6  5  3     81.712
2  6  6  0     83.064
2  8  3  1     84.384
2  6  6  2     85.634
2  7  7  0    100.938
2  7  7  2    103.720
2  8  6  2    105.070
2  9  4  3    106.390
2  6  6  6    107.772
2  7  6  5    109.072
0  7  7  4    111.922
2  8  6  4    113.294
210  4  2    116.244
2  8  7  3    117.594
2  9  6  3    120.646
2  9  7  0    125.178
0  8  8  2    126.798
0  8  8  4    137.102
012  2  0    140.934
0  9  8  3    149.958
1  9  8  3    150.988
```

      PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT

26

```
        1.21031950              9.81695470
        1.12325570              9.83012910
        1.08235430              9.83481970
         .96918944              9.84501580
         .90074096              9.84982800
         .83839262              9.85955600
         .80912364              9.86552280
         .78138079              9.87384990
         .75583984              9.88799320
         .49259600              9.89448530
```

.45316738	9.89900510
.43484372	9.90464690
.41742111	9.91258370
.39969037	9.91689660
.38347666	9.92677600
.34945852	9.92451920
.33380704	9.93983970
.30168885	9.94457200
.28766904	9.95485670
.25748730	9.95961900
.21638113	9.90112820
.20271962	9.89714770
.12771431	9.93077140
.10475551	9.94270790
.06043805	9.89671330
.05621191	9.89784510

LEAST SQUARES ANALYSIS   GAMMA ONE (AGHG) FROM AGCU+HG
A=   .99464364E+01(+OR-   .59223810E-04)
B=   -.97353321E-01(+OR-   .15550680E-03)
Y=B*X+A

. DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
  CUHG FROM AGCU+HG
2 3 1 0   31.142
2 3 2 1   36.964
2 4 1 1   42.046
2 3 3 2   46.568
2 6 0 0   61.200
2 6 3 3   77.480
2 8 1 1   87.020
   PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT
  7
        3.43570420   9.08150200
        2.81302440   9.09888180
        2.40170450   9.11686760
        2.10537170   9.14721850
        1.42133070   9.08637330
         .93599901   9.05237500
         .72832091   9.09645840
    LEAST SQUARES ANALYSIS   CUHG FROM AGCU+HG
    A=   .90815775E+01(+OR-   .54844792E-03)
    B=   .78490269E-02(+OR-   .11513491E-03)
  Y=B*X+A

```
.    DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
     CUHG FROM CU+HG
2 2 2 0    28.156
2 3 1 0    31.318      _¹
2 2 2 2    34.360
2 3 2 1    36.960      _²
2 4 0 0    39.750
2 4 1 1    42.160      _³
2 4 2 0    44.700
2 3 3 2    46.646      _⁴
2 4 2 2    48.804
2 5 1 0    51.124
2 5 2 1    55.058
2 5 3 0    58.752
2 6 0 0    60.830      _⁵
2 6 1 1    62.366
2 6 2 0    64.174
2 5 4 1    65.750
2 6 2 2    67.456
2 6 3 1    69.162
2 4 4 4    70.818
2 5 5 0    72.324
2 6 4 0    74.552
2 7 2 1    75.988      _⁶
2 6 4 2    77.464
2 7 3 0    79.350
2 7 3 2    82.212
2 8 0 0    83.918
2 8 1 1    85.474
2 8 2 0    86.698
2 7 5 2    94.174
2 9 1 0    97.508
2 9 2 1   100.500
2 6 6 4   102.106
2 9 3 0   103.510
2 9 3 2   106.502
0 8 4 4   109.684
0 7 6 5   119.420
0 7 7 4   122.904
0 9 6 1   126.346
0 9 6 3   134.126
0 7 7 6   143.592
```

PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT
40

3.84847890	8.96391700
3.41370540	9.03173220
3.06710840	9.04086420
2.81338890	9.09983180
2.57554400	9.07011560
2.39352570	9.09333380
2.22118480	9.06615030
2.10071840	9.13277500
1.97730440	9.14123330
1.85510230	9.10984230
1.66902480	9.13535580
1.51456810	9.16344050
1.43499810	9.13630220
1.37919530	9.17792850
1.31653390	9.17823490
1.26439530	9.20387700
1.21038140	9.20936040
1.15872360	9.21194530
1.11068760	9.21780810
1.06869720	9.23790820
1.00934680	9.17843610
.97274199	9.20249420
.93638636	9.22009240
.89170665	9.19584730
.82746546	9.23257400
.79108284	9.22394960
.75907030	9.22844880
.73464067	9.26070350
.59856378	9.29604570
.54446273	9.28426320
.49901465	9.29832350
.47576329	9.29835580
.45606443	9.31191160
.41596491	9.32782920
.37599679	9.23089610

```
        .26936318              9.35565040
        .23646581              9.36231840
        .20647794              9.37618530
        .14734038              9.38833370
        .09031024              9.38605860
   LEAST SQUARES ANALYSIS   CUHG FROM CU+HG
   A=    .93386176E+01(+OR-    .85746892E-04)
   B=   -.10397035E+00(+OR-    .34884892E-04)
Y=B*X+A
```

.   DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
     CU FROM CU+HG
2 1 1 1   45.020
2 2 0 0   52.048
2 2 2 0   76.300
2 3 1 1   91.746
2 2 2 2   97.508
2 4 0 0   117.996
0 3 3 1   137.590
1 3 3 1   138.322
0 4 2 0   145.620
1 4 2 0   146.372
     PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT
  10
          2.20072850   3.48763050
          1.80915100   3.51404790
           .96495194   3.52975110
           .64041368   3.56193790
           .54446273   3.55165790
           .28357466   3.59745960
           .12464767   3.60127630
           .12012660   3.60137790
           .08008117   3.60573090
           .07645938   3.60744950
     LEAST SQUARES ANALYSIS   CU FROM CU+HG
     A=   .36036389E+01(+OR-   .25761877E-04)
     B=   -.55237132E-01(+OR-   .26083816E-04)
     Y=B*X+A

.   DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
     CUHG FROM A.S.T.M. X-RAY DATA FILE   4-0811

```
2 2 2 0    26.750
2 3 1 0    29.972
2 2 2 2    32.934
2 3 2 1    35.620
2 4 1 1    40.626
2 3 3 2    45.094
2 4 4 2    58.830
2 6 1 1    60.510
2 6 3 3    74.070
2 5 5 4    83.310
2 8 5 1   101.990
2 9 4 1   108.290
```

     PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT
   12

```
        4.07309840          9.42579120
        3.58814470          9.42741100
        3.22209360          9.42077410
        2.93984490          9.43043440
        2.50709380          9.42135700
        2.19603540          9.42985580
        1.51149180          9.41771640
        1.44693740          9.43156010
        1.02191700          9.40533900
         .80389194          9.42270240
         .47741676          9.41113020
         .39317639          9.41567390
```

    LEAST SQUARES ANALYSIS   CUHG FROM A.S.T.M. DATA FILE 4-0811

A=   .94142934E+01(+OR-   .25075586E-04)
B=   .36471798E-02(+OR-   .45558235E-05)

$Y=B*X+A$

. DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
GAMMA ONE (AGHG) FROM AG+HG

```
2  7  1  0     64.662
2  6  4  0     66.064
2  7  2  1     67.566
2  7  3  2     73.226
2  8  1  1     75.980
2  6  5  3     78.636
2  6  6  0     80.038
2  8  3  1     81.440
2  6  6  2     82.842
2  9  3  2     94.824
2  9  4  1     97.458
2  7  7  2    100.212
2  8  6  2    101.686
2  9  4  3    103.088
2  6  6  6    104.420
2  7  6  5    105.822
2  7  7  4    108.728
2  8  6  4    110.150
2  9  6  1    111.532
210  4  2    113.004
2  8  7  3    114.688
2  9  6  3    117.662
0  8  8  2    122.422
0  7  7  6    124.024
0  9  7  4    134.792
010  5  5    138.850
0  9  8  3    143.306
010  7  3    148.296
110  7  3    149.298
0  9  9  0    154.206
```

   PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT
30

```
        1.30015030           10.19244100
        1.25426930           10.19793000
        1.20698130           10.18770100
        1.04428250           10.17760300
```

```
.97294247          10.17464900
.90839392          10.17911100
.87588240          10.17231000
.84438852          10.16527000
.81386946          10.15809800
.58771795          10.15167300
.54524655          10.15359300
.50326717          10.14765300
.48176904          10.13848000
.46192482          10.13528300
.44360170          10.13755400
.42485901          10.13559600
.38772379          10.12735300
.37036614          10.12650000
.35399238          10.12886600
.33707684          10.12666400
.31837261          10.11343600
.28697393          10.11310100
.24086178          10.09756600
.22643944          10.09719700
.14280891          10.08138400
.11692390          10.07633700
.09180755          10.07045600
.06760875          10.06464600
.06323337          10.06506300
.04406358          10.05740100
```

LEAST SQUARES ANALYSIS   GAMMA ONE (AGHG) FROM AG+HG
A=   .10077265E+02(+OR-   .20020402E-04)
B=   .10388576E+00(+OR-   .48765102E-04)
Y=B*X+A

.   DIFFRACTION DATA INPUT FOR LATTICE PARAMETER CALCULATIONS
     GAMMA ONE (AGHG) FROM MURPHY

```
 2  5  2  1      50.30
 2  6  0  0      55.22
 2  5  4  1      60.090
 2  6  2  2      61.66
 2  6  3  1      63.10
 2  4  4  4      64.70
 2  7  1  0      66.310
 2  6  4  0      67.50
 2  7  2  1      69.20
 2  6  4  2      70.51
 2  7  3  2      74.71
 2  8  1  1      77.51
 2  6  5  3      80.090
 2  6  6  0      81.49
 2  8  3  1      82.89
 2  6  6  2      84.29
 2  7  5  2      85.70
 2  8  4  0      86.910
 2  9  1  0      88.310
 2  9  2  1      90.44
 2  6  6  4      92.30
 2  9  3  0      93.70
 2  9  3  2      96.41
 2  9  4  1      99.20
 2  7  7  2     101.89
 2  8  6  2     103.40
 2  9  4  3     104.71
 2  6  6  6     106.20
 2  7  6  5     107.51
 0  7  7  4     110.30
 1  7  7  4     110.85
 0  8  6  4     111.68
 1  8  6  4     112.10
 010 4  2     114.60
 110 4  2     115.24
```

```
0  8  7  3    116.11
1  8  7  3    116.60
0  9  6  3    119.29
1  9  6  3    119.82
0  8  8  0    120.91
1  8  8  0    121.50
0  8  8  2    123.89
1  8  8  2    124.60
0  8  6  6    126.27
1  8  6  6    126.94
0  8  7  5    128.87
1  8  7  5    129.73
010 6  2    130.70
110 6  2    131.42
0  9  6  5    132.58
1  9  6  5    133.26
0  9  7  4    136.28
1  9  7  4    136.96
```

PARAMETER CALCULATION OUTPUTS,LEAST SQUARE ANALYSIS INPUT

53

```
1.89734970        9.93516000
1.66186850        9.98022080
1.46277760        9.97830630
1.40454030        9.97771810
1.35337540        9.99236750
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1.24639530        9.96700930
1.20902010       10.00587600
1.15759850        9.97609290
1.11947070        9.99419340
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 .93527321       10.00451200
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 .81284128       10.01879200
 .78332975       10.01545700
 .75451060       10.01103200
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.36201233	10.01290400
.35226735	10.02552100
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.31933316	10.02680700
.31238891	10.01597900
.30310339	10.02607400
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.26545223	10.01749900
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.24940824	10.01271000
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.22138472	10.01983800
.20711400	10.06932600
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.17932352	10.01965000
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.16659648	10.02372900
.15817452	10.02475300
.15335464	10.02373000
.13297567	10.02801600
.12861461	10.02924800

LEAST SQUARES ANALYSIS   GAMMA ONE (AGHG) FROM MURPHY

A=   .10040398E+02(+OR-   .13966532E-04)

B=   -.40055300E-01(+OR-   .24551123E-04)

Y=B*X+A